PB85-106243

Abiotic Hydrolysis of Sorbed Pesticides

Colorado School of Mines, Golden

Prepared for

Environmental Research Lab., Athens, GA

Sep 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-106243

EPA-600/D-84-240
September 1984

ABIOTIC HYDROLYSIS OF SORBED PESTICIDES

by

D. L. Macalady
Department of Chemistry and Geochemistry
Colorado School of Mines
Golden, CO 80401
and
N. L. Wolfe
U.S. Environmental Protection Agency
Environmental Research Laboratory
Athens, GA 30613

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GA 30613

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/D-84-240	2.
3. RECIPIENT'S ACCESSION NO. PB85 106243	
4. TITLE AND SUBTITLE Abiotic Hydrolysis of Sorbed Pesticides	5. REPORT DATE September 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) D.L. Macalady and N.L. Wolfe*	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Colorado School of Mines Golden CO 80401 *U.S. Environmental Protection Agency Athens GA 30613	10. PROGRAM ELEMENT NO. CBWD1A
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency--Athens GA Office of Research and Development Environmental Research Laboratory Athens GA 30613	13. TYPE OF REPORT AND PERIOD COVERED Paper
	14. SPONSORING AGENCY CODE EPA/600/01

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The hydrolysis of pesticides that are sorbed to sterilized natural sediments has been investigated in aqueous systems at acid, neutral and alkaline pH's. The results show that the rate constants of pH independent ("neutral") hydrolyses are the same within experimental uncertainties as the corresponding rate constants for dissolved aqueous phase pesticides. Base-catalyzed rates, on the other hand, are substantially retarded by sorption and acid-catalyzed rates are substantially enhanced. A large body of evidence will be presented that substantiates these conclusions for a variety of pesticide types sorbed to several well-characterized sediments. The significance of our results for the evaluation of the effects of sorption on the degradation of pesticides in waste treatment systems and natural water bodies also will be discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 31
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Abiotic Hydrolysis of Sorbed Pesticides

D. L. Macalady
Department of Chemistry and Geochemistry
Colorado School of Mines
Golden, CO 80401
and
N. L. Wolfe
U. S. Environmental Protection Agency
Environmental Research Laboratory
Athens, GA 30613

The hydrolysis of pesticides which are sorbed to sterilized natural sediments has been investigated in aqueous systems at acid, neutral and alkaline pH's. The results show that the rate constants of pH independent ("neutral") hydrolyses are the same within experimental uncertainties as the corresponding rate constants for dissolved aqueous phase pesticides. Base-catalyzed rates, on the other hand, are substantially retarded by sorption and acid-catalyzed rates are substantially enhanced. A large body of evidence will be presented which substantiates these conclusions for a variety of pesticide types sorbed to several well-characterized sediments. The significance of our results for the evaluation of the effects of sorption on the degradation of pesticides in waste treatment systems and natural water bodies will also be discussed.

Introduction

Whether such disposal is intentional or incidental, significant quantities of pesticides and pesticide wastes end up in natural and artificial aquatic systems. Thus, any consideration of the disposal of this broad category of anthropogenic chemicals must include an understanding of the reaction mechanisms and principal pathways for degradation of pesticides in aquatic systems. Of the degradative pathways relevant to such systems, hydrolysis reactions are perhaps the most important type of chemical decomposition process (1-7).

Since many pesticides are compounds of low water solubility, their form in aquatic systems is often dominated not by material in aqueous solution, but rather by material sorbed to suspended or bottom sediments (8-9). Thus, an understanding of the hydrolytic reactions of pesticides which are sorbed to

sediments is crucial for an adequate representation of the dominant chemical degradative pathways for these compounds in aquatic systems.

It is the purpose of this article to summarize the present status of our understanding of the factors governing the rates of hydrolysis of pesticides which are sorbed to sediments. The work reported herein deals specifically with abiotic hydrolysis reactions, which for some pesticides, may be as important or more important than biologically mediated hydrolysis reactions (7, 10-13).

Until recently, no efforts to measure the rates of hydrolytic degradation of sorbed pesticides have been reported. Indeed, it has been widely assumed that hydrolytic reactions are important only in the aqueous phase and that hydrolysis of sorbed pesticides proceeds at an insignificant rate (13).

The only available evidence in the literature which relates, though indirectly, to hydrolysis of sorbed pesticides concerns pesticides in soil systems (see for example 14, 15). Though the results of such studies are not directly applicable to aquatic systems, they do, in general, show that certain pesticides undergo abiotic reactions in soil-sorbed states.

This review, then, reports results of experiments which provide information that can be used to test the hypothesis that hydrolysis reactions proceed at substantially reduced rates when the molecules undergoing hydrolysis are sorbed to sediments. Results are reported for a variety of pesticides and for model compounds that are similar in structural features to pesticides. Included are neutral, base-catalyzed and, to a limited extent, acid-catalyzed hydrolysis reactions.

Preliminary Considerations.

Three general classes of hydrolytic reactions in aqueous solutions have been characterized. In neutral, or pH independent hydrolysis, the rate of disappearance of a pesticide, P, is given by

$$\frac{d[P]}{dt} = - k_1 [P], \qquad (1)$$

where k_1 is the first-order disappearance rate constant. For base-mediated hydrolysis, the corresponding expression is

$$\frac{d[P]}{dt} = -k_B[B][P] = -k_{obs}[P] \qquad (2)$$

where B represents a generalized base. For natural waters and the experimental systems relevant to this report, the only base of significance for such reactions is the hydroxide ion, OH^- (16). In equation 2, k_{obs} represents a pseudo first-order rate constant, valid at fixed pH (or [B]).

Recently reported results for the hydrolysis kinetics of chlorpyrifos (7) suggest that equation 2 may not be a valid representation of alkaline hydrolysis kinetics for at least one class of pesticides (organophosphorothioates). In short, k_B may be pH dependent. However, disappearance kinetics for such molecules are still adequately described at fixed pH by pseudo first-order kinetics.

Acid-catalyzed hydrolysis kinetics are described by the expression

$$\frac{d[P]}{dt} = -k_a[H^+][P] = -k_{obs}[P] \qquad (3)$$

where $[H^+]$ represents the hydrogen ion activity, and k_{obs} the pseudo first-order disappearance rate constant at fixed pH.

For a given pesticide which undergoes hydrolysis, any or all of these hydrolytic pathways may be relevant at various pH's. Organophosphorothioates, for example, have measurable neutral and alkaline hydrolysis rate constants (7). Esters of 2,4-dichlorophenoxyacetic acid (2,4-D), on the other hand, hydrolyze by acid and alkaline catalyzed reactions, but have extremely small neutral hydrolysis rate constants (17). Thus, any study of the hydrolysis of sorbed pesticides must be prefaced by an understanding of the hydrolytic behavior of individual pesticides in aqueous solution.

Another important consideration in investigation of the reaction of sorbed pesticides is the nature of the sorption process itself. Sorption/desorption kinetics and the physicochemical characteristics of the pesticide molecules in the sediment-sorbed state can be expected to influence the kinetic observations made in experimental systems.

Sorption has been commonly described as an equilibrium process, in which the pesticide molecules are rapidly and readily exchanged between the sediment and aqueous phases. In this approach (8), the equilibrium water phase concentration, C_w (expressed relative to suspension volume) is related to the sediment phase concentration, C_s (expressed relative to dry weight sediment), through

$$K_p = C_s/C_w \qquad (4)$$

where K_p is the equilibrium partition coefficient ($L\text{-}g^{-1}$) for the pesticide. C_w is then related to the total concentration of pesticide, C_T, by

$$C_w = \frac{C_T}{1+\rho K_p} \qquad (5)$$

where ρ is the sediment-to-water ratio. K_p has been shown to be directly proportional to the weight fraction of organic carbon in the sediments (O.C.)

$$K_p = (O.C.)\, K_{oc} \qquad (6)$$

For a given pollutant, K_{oc} has been shown in turn to be directly related to the octanol-water partition coefficient of the pesticide (18).

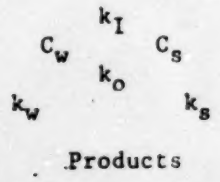
Several investigations have, however, verified the inadequacy of this representation of the sorption process. Variations of "K_p" with sediment concentration (19, 20) have been reported. More importantly, the rate of the sorption process has been shown to be more complex than a simple rapid equilibrium between sediment and aqueous phases (9, 10, 21).

The fact that sorptive equilibrium can be approached quite slowly is illustrated dramatically by data for the system in which chlorpyrifos is sorbed to EPA-14, one of a group of sediments collected and characterized for the U. S. Environmental Protection Agency (22). Figure 1 is a plot of the sediment/aqueous concentration ratio versus time for this system. It is characterized by a rapid sorption process and a much slower sorption process which does not reach equilibrium until about 10 days after initial mixing of the sediment and chlorpyrifos solution.

Though this system is perhaps an extreme example of slow sorption kinetics, it illustrates that the assumption of rapid equilibrium between the sediment and aqueous phases is questionable. The importance of such an observation to the investigation of hydrolysis kinetics in sediment/water systems must be emphasized. Certainly, any model of hydrolysis kinetics in sediment/water systems must include explicit expressions for the kinetics of the sorption/desorption process.

Unfortunately, our present understanding of sorption kinetics is inadequate to allow unambiguous representation of the sorption-desorption process. Clearly the states of sorbed pesticides include fractions which vary in their lability with respect to desorption (9, 10, 21). The fraction of the sorbed molecules in relatively labile and non-labile states is a function of the nature of the pesticide and sediment and the time of contact between the sediment and pesticide solution.

With these limitations in mind, however, we have used the following model to represent the kinetics of the hydrolysis of pesticides in sediment/water suspensions (10)



(7)

Here, k_I represents a pseudo first-order rate constant (linear in sediment concentration) for the sorption process, k_o the

first order rate constant for desorption, k_w the first or pseudo first-order rate constant for hydrolysis of the aqueous (dissolved) pesticide and k_s the corresponding rate constant for hydrolysis of the sorbed pesticide.

This model, in light of the discussion above, is clearly not representative of all of the kinetic processes which are occurring in sediment/water systems containing hydrophobic pesticides. However, it does include at least the more labile fraction of the sorbed pesticide in the overall kinetic model. Complications due to the inadequacy of this representation will be illustrated and discussed below.

Based on this model, the following rate equations relating the hydrolytic degradation of pesticides from sediment water suspensions can be written:

$$\frac{dC_w}{dt} = -(k_w+k_I)C_w + k_o C_s$$

$$\frac{dC_s}{dt} = -(k_s+k_o)C_s + k_I C_w \qquad (8)$$

$$\frac{dPr}{dt} = k_s C_s + k_w C_w$$

where Pr represents the concentration of products in the aqueous phase. Products are uniformly more hydrophilic than the parent pesticide molecules, making sorption of product molecules a relatively unimportant consideration.

To the extent that overall disappearance kinetics in such systems are pseudo first order, we may also write

$$\frac{dC_T}{dt} = -k_{obs} C_T \qquad (9)$$

Note that if hydrolysis of sorbed molecules is unimportant and sorption/desorption is fast relative to hydrolysis, then, from equations 5 and 9,

$$k_{obs} = k_w/(1+\rho K_p) \qquad (10)$$

Experimental Considerations

Details concerning the experimental procedures used to obtain the data upon which the results discussed below are based have been presented elsewhere (7, 10-12, 17). Three types of experiments are involved.

First, determination of hydrolysis kinetics for each compound in sediment-free distilled, buffered distilled or natural water systems were measured. Using sterile techniques, concentrations of the parent compounds were determined as a

function of time. Generally, these experiments were conducted by withdrawing aliquots of an aqueous solution of the compound from the temperature-controlled reaction flask, extracting the parent compound from the aliquot using an organic solvent (usually iso-octane) and determining concentrations of the parent compound using gas-liquid chromatography.

Such experiments were repeated for each compound at a variety of pH's and temperatures so that pH-rate constant profiles and activation energies could be obtained. Extraneous experimental complications such as sorption of the compound to container walls, incomplete extraction from aqueous solutions and possible catalysis by metal ions in solution were carefully monitored and accounted for in the final determination of aqueous phase hydrolysis rate constants. Of these possibilities, only sorption to container walls was observed to have a measurable effect on the experimental data.

In addition, most of these aqueous phase experiments included product identification using gas chromatographic-mass spectrometric (GC-MS) or liquid chromatographic-MS techniques. Product analyses were used to verify that disappearance kinetics were indeed due to hydrolysis reactions.

In a second class of experiments, detailed studies of disappearance kinetics in sediment-water systems were performed. A series of centrifuge tubes was assembled containing identical concentrations of parent compound and identical sediment-to-water ratios.

The tubes were gently agitated at constant temperature and sacrificed at regular time intervals. Each tube was centrifuged and the bulk of the water phase separated from the sediment phase. The aqueous and sediment phases were then separately analyzed for the remaining concentrations of parent compound. Careful tests were conducted to assure complete extraction of the compound from the two phases (10). Thus, the concentrations remaining in each phase could be separately determined as a function of time.

The third class of experiments was similar to the second, except that the centrifugation step was omitted and only the total parent compound concentration in the sediment-water systems was determined as a function of time.

Finally, several types of auxilliary experiments were performed during various phases of these investigations. Included were purity checks on parent compounds, determinations of K_p values for selected compounds on various sediments, investigations of the effect of pH on measured K_p's, verification of the validity of pH measurements in dilute sediment-water slurries, elimination of the possibility of buffer catalysis of hydrolysis reactions in our systems, and qualitative product analyses from sediment/water hydrolysis studies.

All sediments used in the studies reported in this article were selected from a group of well-characterized soil and sediment samples which were collected and air-dried for the U. S. Environmental Protection Agency by Hassett and co-workers (22). The characteristics of several of these are outlined in Table I.

Table I. Characteristics of Sediments Used in These Studies

	Sediment				
	EPA-12	EPA-13	EPA-14	EPA-23	EPA-26
pH (1:2)	7.55	6.74	4.3	7.1	8.1
CEC (meq/100g)	13.53	11.9	18.9	31.15	20.86
total N (%)	0.214	0.167	0.064	0.195	0.152
organic carbon (%)	2.33	3.04	0.48	2.38	1.48
sand/silt/ clay (%)	0/35/64	20/53/27	2/64/34	17/69/14	2/43/55
K_p for chlopyrifos:					
calculated (from K_{ow})[a]	465	608	96	475	300
measured (± S.D.)	-	-	83 ± 6	403 ± 92	307 ± 96

[a]Reference 22

Results and Discussion

Neutral Hydrolysis Studies. Investigations of neutral (pH-independent) hydrolysis kinetics in sediment/water systems were conducted for three organophosphorothioate insecticides (chlorpyrifos, diazinon and Ronnel), 4-(p-chlorophenoxy)butyl bromide, benzyl chloride, and hexachlorocyclopentadiene.

1. Chlorpyrifos, O-O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate, is the compound for which the most exhaustive kinetic investigations were conducted (10). The kinetics of the hydrolysis as a function of pH in distilled and buffered distilled water systems is summarized by the pH-rate profile shown in Figure 2 (7). The value, $k_{obs}=(6.22\pm0.09) \times 10^{-6}$ min^{-1} is the neutral hydrolysis rate constant for chlorpyrifos in distilled water at 25°C.

Values at 25°C for the hydrolysis rate constants of chlorpyrifos in sterilized natural waters and in water isolated from a 25 g/l slurry of EPA-14 in distilled water (stirred for 1 week prior to separation of the sediment and water phases) are

shown in Table II. The variability in these data and the apparent increase in the rate constants from distilled to natural waters are unexplained. Biological, trace metal and glass-surface catalysis have been eliminated as possible sources of this variability and rate enhancement. Biological degradation was determined (7) to be unimportant for chlorpyrifos in our systems, so sterility is not a factor. A value of k_{obs}=1.0 x 10^{-5} min^{-1} was selected as a reasonable approximation of the hydrolysis rate constant in the aqueous phases of the sediment-water systems used in these studies.

Table II. Ranges of Measured Rate Constants for the Disappearance of Chlorpyrifos from Natural Water Samples at 25°C

Samples	Rate Constants[a]
Oconee River water (20)[b]	(0.71 - 4.00) x 10^{-5} min^{-1}
Hickory Hills Pond (12)[b]	(1.00 - 3.90) x 10^{-5} min^{-1}
EPA - 14 supernatant (6)[b]	(0.64 - 0.97) x 10^{-5} min^{-1}

[a]Ranges shown represent a composite of autoclaved and filter sterilized trials, along with trials involving non-sterilized waters. No bacterial effects are in evidence. Effects of pH are unimportant in these waters. Metal catalysis is not a factor. For a detailed analysis of the data including error analysis, see reference 7.
[b]Number of kinetic runs in parentheses.

The data from a representative study of the disappearance of chlorpyrifos from an EPA-14 sediment/water system (ρ=0.20, fraction sorbed = 0.94) is illustrated in Figure 3. Comparison with Figure 1 shows that once sorptive equilibrium is achieved (t>14,000 minutes) the disappearance rate is first order for both the water and sediment phases. Also, the aqueous disappearance rate constant calculated from the slope of the linear portion of the natural log aqueous concentration versus time plot is 0.5±0.2 x 10^{-5} min^{-1}, which is similar to the values measured in sediment-free EPA-14 supernatant (Table II). A plot summarizing two experiments using EPA-23 sediment is shown in Figure 4. The value of k_w calculated from the natural log water concentration vs. time plot in this figure is (1.9±0.2) x 10^{-5} min^{-1}.

Data from these studies were analyzed by a computer using equations 8 based on our simple kinetic model for the sediment/water systems (eqn. 7). The computer program (23) uses concentrations of chlorpyrifos in the water and sediment phases and product concentrations (obtained by difference) as a

Reproduced from best available copy.

function of time to calculate values for any three of the rate constants k_I, k_o, k_w and k_s. For the purposes of our calculations, a "known" value of 1.0×10^{-5} min^{-1} for k_w was used to enable calculation of k_I, k_o and k_s. The results of these calculations are shown in Table III. Also shown in Table III are values for k_{obs}, the overall chlorpyrifos disappearance rate constant, and a value calculated for k_{obs} using equation 10, which is based on $k_s=0$, i.e. no hydrolysis of sorbed chlorpyrifos.

Table III. Observed and Calculated Values of Rate Constants (min^{-1}) for Chlorpyrifos in Sediment/Water Systems at Non-adjusted pH's.[a]

	EPA 14	EPA 23	EPA 23
sediment/ water (ρ)	0.20	0.016	0.016
fraction sorbed	0.94	0.87	0.87
sterile?	yes	no	yes
k_{obs}	1.0×10^{-5}	1.7×10^{-5}	1.6×10^{-5}
k_{obs} (calc.)[b]	6.0×10^{-7}	1.3×10^{-6}	1.3×10^{-6}
k_I	$(6 \pm 2) \times 10^{-3}$	$(4 \pm 1) \times 10^{-3}$	$(4 \pm 1) \times 10^{-3}$
k_o	$(6 \pm 2) \times 10^{-4}$	$(9 \pm 3) \times 10^{-4}$	$(4 \pm 2) \times 10^{-4}$
k_w (fixed)[c]	1.0×10^{-5}	1.0×10^{-5}	1.0×10^{-5}
k_s	$(6.9 \pm 0.9) \times 10^{-6}$	$(1.8 \pm 0.1) \times 10^{-5}$	$(1.2 \pm 0.1) \times 10^{-5}$
pH (H_2O phase)	4.1 ± 0.4	7.2 ± 0.2	7.4 ± 0.4

[a] (See text for Symbol Definitions).
[b] Assuming sediment/water equilibrium, no hydrolysis in the sorbed state, and $k_w = 1.0 \times 10^{-5}$, $k_{obs} = k_w/(1+\rho K_p)$.
[c] For computer model calculations.

Several features of these calculations are important. First, the computer calculated uncertainties shown for the calculated values of k_I, k_o and k_s are an indication that the model has considerable validity for describing the kinetics of the system, at least over one half-life in the disappearance of chlorpyrifos. Second, the values of k_o and k_I are all similar and their magnitude indicates that in this case the assumption of rapid sorption/desorption kinetics compared to hydrolysis is valid.

More importantly, the calculated values of k_s are all similar in magnitude to k_w. Coupled with the fact that the

values calculated for k_{obs} assuming no sediment phase hydrolysis are all considerably lower than the actual values for k_{obs}, these k_s values indicate that neutral hydrolysis of chlorpyrifos in the sorbed state proceeds at a rate that is the same as the disappearance rate in the aqueous phase.

2. Diazinon and Ronnel. The conclusion that neutral hydrolysis of sorbed chlorpyrifos is characterized by a first-order rate constant similar to the aqueous phase value is strengthened and made more general by the results for diazinon, 0,0-diethyl 0-(2-iso-propyl-4-methyl-6-pyrimidyl) phosphorothioate, and Ronnel, 0,0-dimethyl 0-(2,4,5-trichlorophenyl) phosphorothioate (10). The results for the pH independent hydrolysis at 35°C for these compounds in an EPA-26 sediment/water system (ρ=0.040) are summarized in Table IV. Because the aqueous (distilled) values of k_w for diazinon and Ronnel are similar in magnitude to the value for chlorpyrifos, and because these values were shown by the chlorpyrifos study to be slow compared to sorption/desorption kinetics, computer calculations of k_s were not deemed necessary and were not made for these data.

Table IV. Experimental Values for Neutral Hydrolysis Disappearance Rate Constants (min^{-1}) in an EPA 26 Sediment/Water System for Diazinon and Ronnel at 35°C[a]

	Diazinon	Ronnel
sediment/water(ρ)	0.040	0.040
fraction sorbed	0.64	0.96
k_{obs}	$(3 \pm 1)\times10^{-5}$	$(2.7 \pm 0.4)\times10^{-5}$
k_{obs} (calculated)[b]	1.3×10^{-5}	2.3×10^{-6}
k_w (distilled)	$(1.2 \pm 0.2)\times10^{-5}$	$(2.0 \pm 0.2)\times10^{-5}$
k_w (observed)	$(3.8 \pm 0.6)\times10^{-5}$	$(3.8 \pm 1.8)\times10^{-5}$
k_s	$(2.9 \pm 0.5)\times10^{-5}$	$(2.6 \pm 0.3)\times10^{-5}$

[a]Symbols Defined in text.
[b]Assuming sediment/water equilibrium, no hydrolysis in the sorbed state and $k_w = 3 \times k_w$ (distilled)-see discussion. $k_{obs} = k_w/(1 + \rho K_p)$.

Again the values of k_s, calculated from the log C_s vs. time plots, were similar in magnitude to the value of k_w calculated from the log C_w vs. time plots. Also the values of k_{obs} calculated from the k_s=0 assumption implicit in equation 10 were lower than the experimental k_{obs} values. This latter effect is less dramatic for diazinon since its lower K_p value results in an equilibrium fraction sorbed of only 0.64. Note also that the

values for k_w are 2-3 times the distilled water values. This observation is also consistent with the rate enhancements observed for chlorpyrifos in natural (cf. distilled) waters.

Thus, for chlorpyrifos, diazinon, Ronnel (and by extension, other organophosphorothioate pesticides), neutral hydrolysis proceeds at similar rates in both the aqueous and sediment phases of sediment/water systems.

3. Experiments on the hydrolysis of 4-(p-chlorophenoxy) butyl bromide, (PCBB) which proceeds via an S_N2 substitution mechanism (11) were similar in design and data analysis procedures to the chlorpyrifos experiments detailed above. Results from a study at 35°C using EPA-12 sediment with 80% of the compound in the sorbed state are illustrated in Figure 5. Calculated and observed values from this study, using the distilled water value for k_w of $(7.9\pm0.5\times10^{-5})$ min^{-1} as a "known" value for computer calculations are:

$$k_I = 8.1 \times 10^{-5} \text{ min}^{-1}$$
$$k_o = 1.6 \times 10^{-5} \text{ min}^{-1}$$
$$k_s = 5.1 \times 10^{-5} \text{ min}^{-1}$$

Again, the value of k_s is similar in magnitude to the value of k_w. Other studies using EPA-12 (80-95% sorbed) at 25°C and EPA-10 (90% sorbed) at 35° also indicate similar values for k_s and k_w.

Several features of the PCBB experiments are different than those for chlorpyrifos. The hydrolysis reaction proceeds via a different mechanism. The rate enhancements observed for chlorpyrifos in natural waters and the aqueous phases of the sediment/water systems (as compared to sterile distilled water) are not observed for PCBB. The values of k_I and k_o calculated for PCBB are slower than those for chlorpyrifos and similar in magnitude to the hydrolysis rates.

In spite of these differences, neutral hydrolysis is still characterized by similar rate constants for both sediment-sorbed and aqueous PCBB.

4. Benzyl chloride hydrolysis proceeds via a third mechanism (S_N1). Results of studies of benzyl chloride hydrolysis (11) in distilled water and EPA-13 and EPA-2 sediment/water systems are summarized in Table V. Results for this compound include only overall first-order disappearance rate constants, but the data clearly show that the hydrolysis rate is independent of the fraction sorbed to sediment. Thus, the conclusion is again made that neutral hydrolysis proceeds via similar rate constants in both the aqueous and sediment-sorbed phases.

Table V. Hydrolysis of Benzyl Chloride in Sediment/Water Systems at 25°C

k_{obs}, $min^{-1} \times 10^3$	Sediment to Water Ratio, ρ(Sed. #)	Fraction Sorbed
1.18 ± 0.05	0	0
1.13 ± 0.03	0	0
1.1 ± 0.1	0.025 (EPA 13)	0.15
1.4 ± 0.1	0.05 (EPA 13)	0.25
1.15 ± .05	1.0 (EPA 2)	0.87
1.10 ± .08	1.0 (EPA 2)	0.87

5. The hydrolysis of hexachlorocyclopentadiene (HEX) represents a fourth hydrolysis mechanism (S_N2'). Studies of the overall disappearance kinetics of HEX from sterile distilled water and EPA-13 sediment/water systems (12) are summarized in Table VI. Again, the rate constants are essentially independent of the sediment concentration and therefore independent of the fraction of the HEX which is sorbed to the sediment. This indicates that neutral hydrolysis of HEX is also characterized by similar rate constants for both the sediment-sorbed and aqueous phases.

Table VI. Hydrolysis of Hexachlorocyclopentadiene in EPA-13 Sediment/Water Systems at 30°C

Sediment to Water Ratio, ρ	k_{obs}, $min^{-1} \times 10^5$
0	9 ± 3
0.05	21 ± 2
0.10	26 ± 2
0.15	27 ± 4
0.20	22 ± 2
0.40	16 ± 1
1.0	20 ± 2
2.0	13 ± 2

In summary, neutral hydrolysis rate constants for six different compounds which hydrolyze by four different hydrolysis mechanisms were determined in sediment/water systems using seven

different sediments. Sediment to water ratios varying from $5x10^{-4}$ to 2.0 were used. Yet, in each case, neutral hydrolysis of the sorbed compounds was shown to be characterized by rate constants which were very nearly equal to the rate constants for hydrolysis in the aqueous phase of these systems. The conclusion is that neutral hydrolysis reactions are not quenched when the molecules undergoing hydrolysis are sorbed to sediments. In fact the rate of neutral hydrolytic reactions appears to be unaffected by sorption.

Alkaline Hydrolysis Studies. Alkaline catalyzed hydrolysis kinetics in sediment/water systems have been investigated for chlorpyrifos and the methyl and n-octyl esters of 2,4-dichlorophenoxyacetic acid (2,4-D).

1. Chlorpyrifos. As was the case for the neutral hydrolysis studies, the most detailed kinetic investigations of alkaline hydrolysis kinetics in sediment/water systems have been conducted using chlorpyrifos (10). As can be seen from Figure 2, alkaline hydrolysis of chlorpyrifos is not second-order, so the value selected for k_w cannot be calculated from the pH and a second-order rate constant. Nevertheless, since aqueous kinetics at alkaline pH's for chlorpyrifos was always pseudo-first order, careful pH measurements and Figure 2 can be used to select accurate values for k_w at any pH.

A preliminary consideration for studies at alkaline pH's is the effect of pH on K_p values and on sorption/desorption rate constants. Studies using chlorpyrifos and EPA-26 (ρ=0.0150) indicate no measurable effects on K_p over the pH range 5.5-10.8 (K_p=250±37 for five determinations). Kinetic effects are also minor, as illustrated by the similarity in the calculated values of k_T and k_o for EPA-23 at pH's of 7.2 and 7.4 (Table III) and 10.67 (Table VII).

Two types of investigations of the alkaline hydrolysis of chlorpyrifos in sediment/water systems were made, all at pH's between 10.6 and 10.8. First, studies were conducted in which the pH was adjusted (using a carbonate buffer) immediately upon mixing the sediments (EPA-23 and EPA-26) with the chlorpyrifos solution. Second, a study using EPA-26 was made in which the alkaline buffer was not added until three days after mixing the sediment with the chlorpyrifos solution. Three days represents a time which is long with respect to the achievement of sediment-water equilibrium for this system, yet short compared to the neutral hydrolysis half life (~50 days).

Table VII. Experimental and Calculated Values of the Rate Constants for the Alkaline Hydrolysis of Chlorpyrifos in Sediment/Water Systems[a]

	EPA 23	EPA 26
pH	10.67 ± 0.04	10.60 ± 0.04
ρ	0.019 ± 0.001	0.031 ± 0.001
K_p	453 ± 59	191 ± 4
ave fr. sorbed	0.90	0.85
k_{obs}	$(1.05 \pm 0.11)\times10^{-4}$	$(1.10 \pm 0.04)\times10^{-4}$
k_{obs}(calculated)[b]	5.0×10^{-5}	6.2×10^{-5}
k_I	$(1.3 \pm 0.8)\times10^{-3}$	$(2.5 \pm 0.9)\times10^{-2}$
k_o	$(1.8 \pm 1.1)\times10^{-4}$	$(4.4 \pm 1.7)\times10^{-3}$
k_w(fixed)[c]	4.8×10^{-4}	4.3×10^{-4}
k_s	$(7.1 \pm 0.8)\times10^{-5}$	$(4.1 \pm 0.3)\times10^{-5}$

[a]Symbols defined in the text. No pre-equilibrium between sediment and chlorpyrifos prior to pH adjustment.
[b]Assuming sediment/water equilibrium, no hydrolysis in the sorbed state, $k_{obs}(calc.) = k_w/(1+\rho K_p)$.
[c]For computer calculations. The value of k_w is the expected distilled water hydrolysis rate constant at this pH.

In the first type of study, pseudo first-order kinetics were observed in both the sediment and aqueous phases from t=0 through two half-lives in overall chlorpyrifos disappearance (total time ~8 days). For these studies, computer calculations using the model illustrated in equations 7 were again used to calculate values for k_I, k_o and k_s, assuming a value of k_w equal to the pseudo first-order rate constant in distilled water buffered to the same pH. Values were also calculated for k_{obs} assuming k_s=0 (equation 10) for comparison to the experimental k_s values. The results of these calculations are shown in Table VII.

The contrast between these alkaline hydrolysis results and the neutral hydrolysis results is striking. The calculated values of k_s are lower by factors of 7-10 than the corresponding k_w values. The values calculated for k_{obs} assuming k_s=0 are only 1.8-2.1 times smaller than the experimental k_{obs} values (cf. calculated values 12-17 times lower than observed for neutral hydrolysis at similar fractions sorbed).

These results, therefore, show that alkaline hydrolysis is considerably slowed when the chlorpyrifos is sorbed to sediments.

The results from the study featuring sediment-chlorpyrifos equilibration prior to pH adjustment (Figure 6) are

qualitatively different than those from the studies without pre-equilibration. Attempts to fit these data to our simple kinetic model gave a very poor fit. The model is clearly inadequate in this case. Though this is a very limited data set, the kinetics appear to follow an initial disappearance of chlorpyrifos dominated by alkaline hydrolysis of the aqueous phase material and desorption of a fraction of the sorbed material. Through approximately one half-life, k_{obs} is 2×10^{-4} min^{-1}, a value similar to the k_{obs} measured for the EPA-26 study without pre-equilibration (1×10^{-4} min^{-1}). Subsequently, however, k_{obs} falls to 5×10^{-5} min^{-1}, a number quite similar to the k_s value calculated for the parallel study without pre-equilibration (4×10^{-5} min^{-1}).

These observations, though tentative, suggest the existence of a substantial fraction of the sorbed material which is considerably less labile with respect to desorption than the material initially sorbed to the sediments. Further study of these effects is clearly needed.

2. Esters of 2,4-D. Studies of the alkaline hydrolysis of the methyl and n-octyl esters of 2,4-D in sediment/water systems (24), though less detailed than the chlorpyrifos studies, show similar effects. Results from investigations using EPA-13 at pH's near 10 for the methyl and octyl esters of 2,4-D are summarized in Figure 7. Under the conditons in these experiments, the fractions of the methyl and octyl esters which are sorbed to the sediment are 0.10 and 0.87, respectively. The aqueous hydrolysis half-lives of the methyl and octyl esters at pH=10 are 3.6 and 27 minutes, respectively. In the sediment/water system, the methyl ester, which is mainly in the dissolved phase, hydrolyzes at a rate similar to that expected for the sediment-free system at the same pH. The octyl ester, on the other hand, hydrolyses at a rate which is considerably retarded (and non-first-order) when compared to the expected aqueous phase rate. Though the data are less detailed and do not permit calculations similar to those conducted for chlorpyrifos, it is clear that the effect of sorption is to considerably slow the alkaline hydrolysis rate.

Studies of the disappearance of the octyl ester at pH 9.8 in sediment/water systems aged 3 days prior to pH adjustment are summarized in Figure 8. For the systems with ρ=0.013 and 0.005 (fractions sorbed = .978 and .945) the rate is pseudo first order, but the rate constant is 10^4 times smaller than the aqueous value (1.6×10^{-1} min^{-1}) at this pH. As was suggested for chlorpyrifos, this k_{obs} value may be characteristic of the actual value of k_s. At ρ=0.001, (fraction sorbed = 0.78), the disappearance kinetics is not first order, but shows rapid disappearance of the aqueous ester, followed by disappearance of the sorbed ester at a rate similar to the studies with higher sediment to water ratios.

Based on experiments for these three compounds, it is clear that the alkaline hydrolysis of sorbed molecules is substantially retarded with respect to the rate for dissolved molecules. The extent of this retardation cannot be quantitatively discussed at this time, however, due to lack of a sufficiently broad set of detailed experimental data.

3. Acid Hydrolysis. Considering the observed results for neutral and alkaline hydrolysis, it is interesting to speculate as to the expected effects of sorption on acid-catalyzed hydrolysis. Since most sediments are of predominantly clay mineralogy, sediment grains exhibit generally negative surface changes at pH's common in natural waters (25). When this is the case, one would expect the concentration of negative ions such as OH^- to be lower near the sediment particle surface. In addition, the (acidic) functional groups of the organic matter associated with the sediments would be expected to be negatively charged at alkaline pH's. These effects alone might be expected to reduce the rate of alkaline hydrolytic processes occuring at these surfaces.

Also, recall that alkaline hydrolysis of organophosphorothioates has been shown to involve a negatively-charged intermediate (v.s. and 7). Such an intermediate would be expected to be less stable in the negatively charged environment of the sediment particle surface.

On the other hand, the concentration of positive ions, including H_3O^+, near sediment particle surfaces would be expected to be enhanced relative to the bulk solution concentrations. From this consideration, we would predict that acid-catalyzed hydrolysis reactions should occur at enhanced rates for sorbed molecules.

Unfortunately, there is presently only a very tentative bit of evidence available to substantiate this prediction. In one experiment at an acid pH, the overall rate of hydrolysis of the n-octyl ester of 2,4-D was measured in a sediment/water slurry in which a substantial fraction of the ester was sorbed. The rate was observed to be substantially faster than the predicted aqueous phase rate. Though this is an indication that the above prediction is correct, much more experimental work is needed to substantiate and quantify this predicted rate enhancement.

Summary and Conclusions

The hypothesis that hydrolysis of sorbed molecules occurs at rates insignificant with respect to aqueous phase hydrolysis has been demonstrated to be incorrect for neutral (pH-independent) hydrolysis reactions. The rate-constants for sorbed state neutral hydrolysis are, on the contrary, similar in magnitude to those for hydrolysis in the aqueous phase.

The hypothesis has been shown to be more nearly correct for alkaline hydrolysis reactions, since significant rate

retardations, corresponding to greatly reduced rate constants for sorbed molecules, occur when substantial fractions of the hydrolyzing molecules are sorbed to sediments.

Inadequate understanding of the kinetics of the sorption/desorption process detracts from our ability to completely understand the effects of sorption on hydrolytic rates, and more research is needed in this regard.

Limited experimental evidence and theoretical considerations suggest that acid-catalyzed hydrolysis rates are subsantially enhanced for sorbed molecules. Much more experimental evidence is necessary, however, to verify this effect.

These conclusions have several implications for pesticide waste disposal considerations. For incidental or accidental disposal of pesticides in natural aquatic systems, the results suggest that model calculations using aqueous solution values for abiotic neutral hydrolysis rate constants can be used without regard to sorption to sediments. For alkaline hydrolysis, on the other hand, models must explicitly include sorption phenomena and the corresponding rate reductions in order to accurately predict hydrolytic degadation.

The limited acid-hydrolysis results, if substantiated, have broader implications. They suggest that rapid hydrolysis of pesticide wastes in acidified artificial sediment/water slurries may be an attractive method for the intentional disposal and degradation of pesticide wastes.

Acknowledgments

Most of the work reviewed in this article was performed at the U. S. Environmental Research Laboratory in Athens, GA. Support for Donald Macalady's work at this laboratory was provided by a Senior Associateship award from the National Rsearch Council.
NOTE: Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U. S. Environmental Protection Agency.

Literature Cited

1. Wolfe, N.L.; Zepp, R.G.; Paris, D.F. Water Research, 1978, 12, 561.
2. Wolfe, N.L.; Burns, L.A.; Steen, W.C. Chemosphere, 1980, 9, 393.
3. Wolfe, N.L.; Zepp, R.G.; Doster, J.C.; Hollis, R.C. J. Agric. Food Chem., 1976, 24, 1041.
4. Wolfe, N.L.; Zepp, R.G.; Paris, D.F. Water Reserch, 1978, 12, 565.
5. Maquire, R.J.; Hale, E.J. J. Agric. Food Chem., 1980, 28, 372.
6. Ou, L.T.; Gancarz, D.H.; Wheeler, W.B.; Rao, P.S.C.; Davidson, J.M. J. Environ. Quality, 1982, 11, 293.
7. Macalady, D.L.; Wolfe, N.L., J. Agric. Food Chem., 1983, 31, 1139.
8. Karickhoff, S.W.; Brown, D.S.; Scott, T.A. Water Research, 1979, 13, 241.
9. Karickhoff, S.W. In Contaminants and Sediments, Baker, R.A., Ed. Ann Arbor Science, Ann Arbor, MI, 1980; Vol. 2, Chapter II.
10. Macalady, D.L.; Wolfe, N.L. "Effects of Sediment Sorption on Abiotic Hydrolyses: I. Organophosphorothioate Esters", submitted to Environ. Sci. Technol., 1983.
11. Pierce, J.H.; Wolfe, N.L. "Effects of Sediment Sorption on Abiotic Hydrolyses: II. 4-(p-chlorophenoxy) butyl bromide and Benzyl Chloride", paper in preparation, 1984.
12. Wolfe, N.L.; Zepp, R.G.; Schlotzhauer, P.; Sink, M. Chemosphere 1982, 11, 91.
13. Wolfe, N.L.; Zepp, R.G.; Paris, D.F.; Baughman, G.L.; Hollis, R.C. Environ. Sci. Technol. 1977, 11, 1077.
14. Sethunan, N.; MacRae, I.C., J. Agric. Food Chem. 1969, 17, 221.
15. Mingelgrin, U.; Saltzman, S.; Yaron, B. Soil Sci. Soc. Am. J. 1977, 41, 519.
16. Perdue, E.M.; Wolfe, N.L. Environ. Sci. Technol. 1983, 11, 635.
17. Wolfe, N.L., U.S. Environmental Protection Agency, Athens, GA. Unpublished results, 1982.
18. Karickhoff, S.W. Chemosphere, 1981, 10, 833.
19. O'Connor, D.J.; Connolly, J.P. Water Research, 1980, 14, 1517.
20. Voice, T.C.; Rice, C.P.; Weber, W.J., Jr. Environ. Sci. Technol., 1983, 17, 513.
21. Miller, C.T.; Weber, W.J., Jr. 186th National Meeting of the American Chemical Society, Washington, D.C., August, 1983; Abstr. PEST 73.
22. Hassett, J.J.; Means, J.C.; Banwort, W.L.; Wood, S.G. "Sorption Properties of Sediments and Energy Related

Pollutants"; U.S. Environmental Protection Agency, Athens, Georgia. EPA-600/3-80-041, 1980.
23. Knott, G.; Reece, D. "MLAB", Division of Computer Research and Technology, National Institute of Health, Bethesda, MD 20014, 7th ed., 1977.
24. Wolfe, N.L. "Effects of Sediment Sorption on Abiotic Hydrolyses: III. Carboxylic Acid Esters", paper in preparation, 1984.
25. Stumm, W.; Morgan, J.J. "Aquatic Chemistry", 2nd Ed., John Wiley & Sons, New York, 1981; Ch. 10.

LIST OF FIGURES

1. Kinetics of the sorption of chlorpyrifos to EPA-14 sediment, ρ = 0.20, t = 25°C.

2. pH-rate constant profile for chlorpyrifos in distilled water at 25°C.

3. Chlorpyrifos disappearance from an EPA-14 sediment/water system, ρ = 0.20, t = 25°C.

4. Chlorpyrifos disappearance from EPA-23 sediment/water systems, ρ = 0.016, t = 25°C.

5. PCBB disappearance from a sterilized EPA-12 sediment/water system, ρ = 0.050, t = 35°C.

6. Chlorpyrifos disappearance from an EPA-26 sediment/water system equilibrated for three days prior to pH adjustment to 10.6; ρ = 0.031, t = 25°C.

7. Alkaline hydrolysis of the 2,4-D methyl ester (pH 10.01) and 2,4-D n-octyl ester (pH 10.12) from heat-sterilized EPA-13 sediment/water systems.

8. Alkaline hydrolysis of the 2,4-D n-octyl ester (pH 9.8) in EPA-13 sediment/water systems equilibrated 3 days prior to pH adjustment.

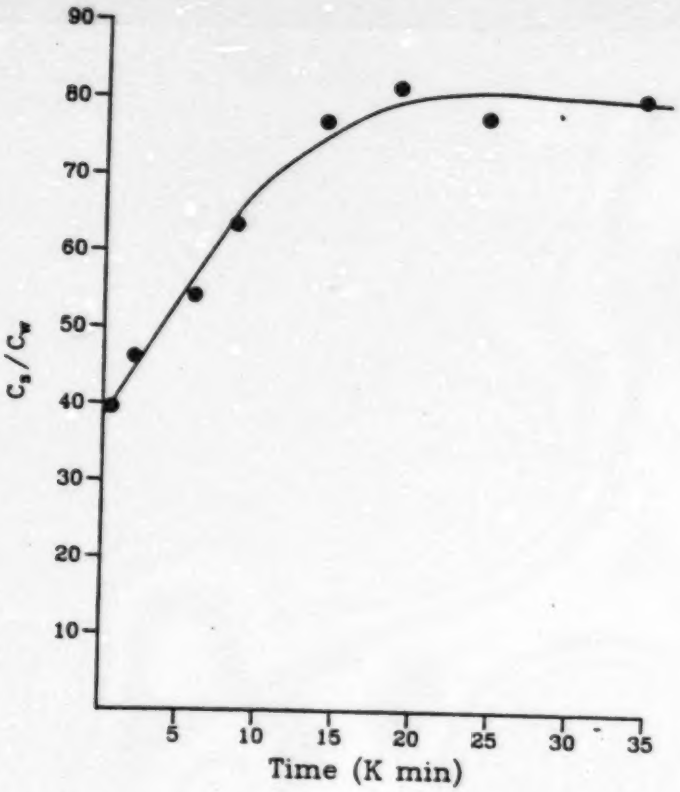


Figure 1.

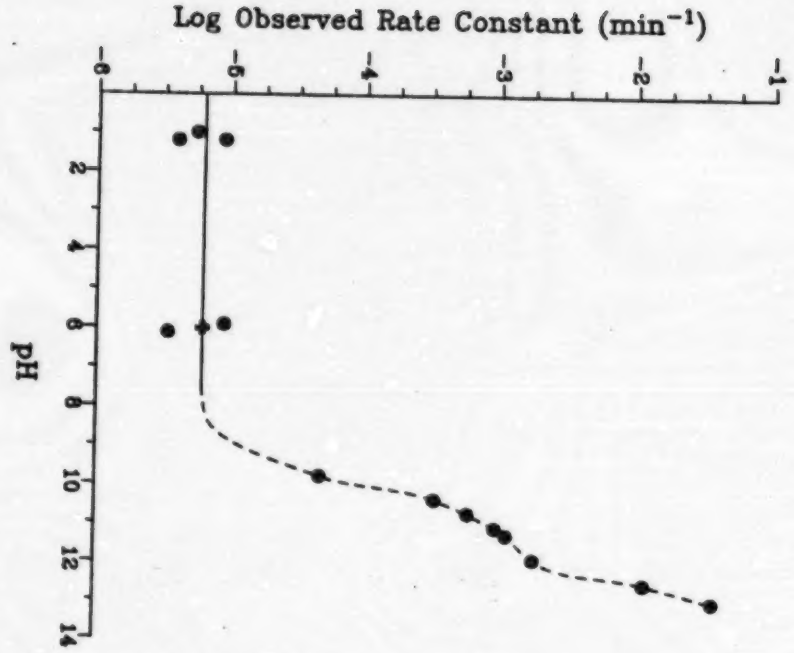


Figure 2.

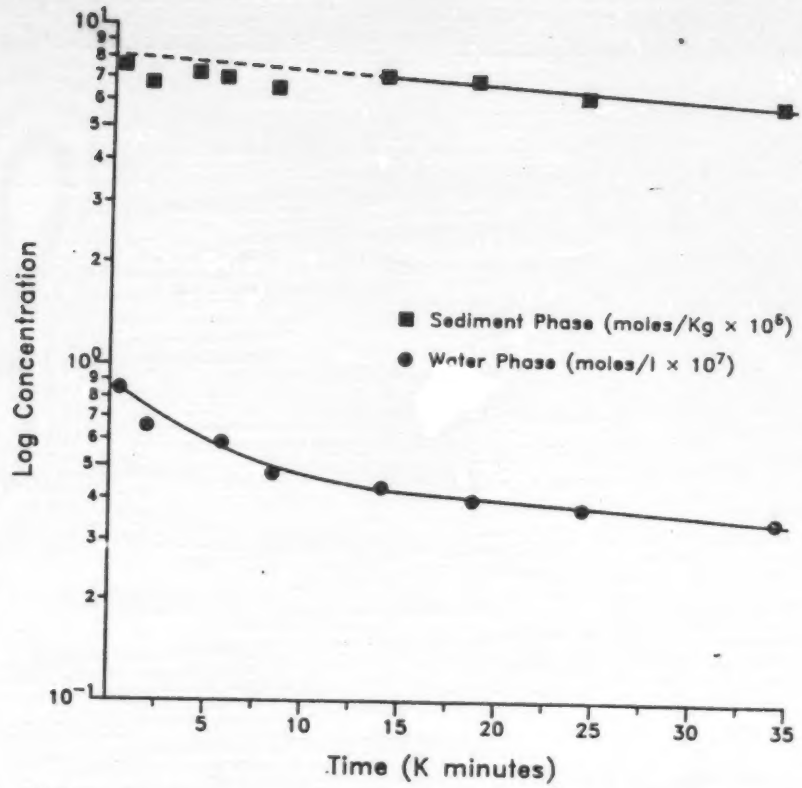

Log Concentration
Time (K minutes)
Sediment Phase (moles/Kg × 10⁵)
Water Phase (moles/l × 10⁷)

Figure 3.

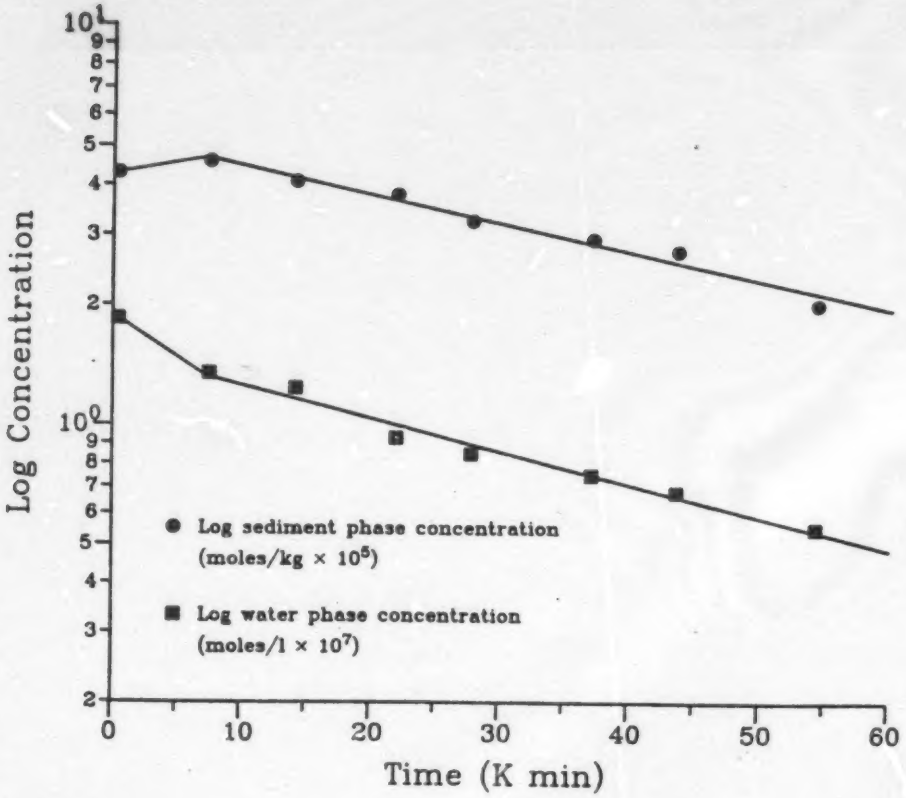

Log Concentration
Time (K min)
Log sediment phase concentration
(moles/kg × 10^5)
Log water phase concentration
(moles/l × 10^7)

Figure 4.

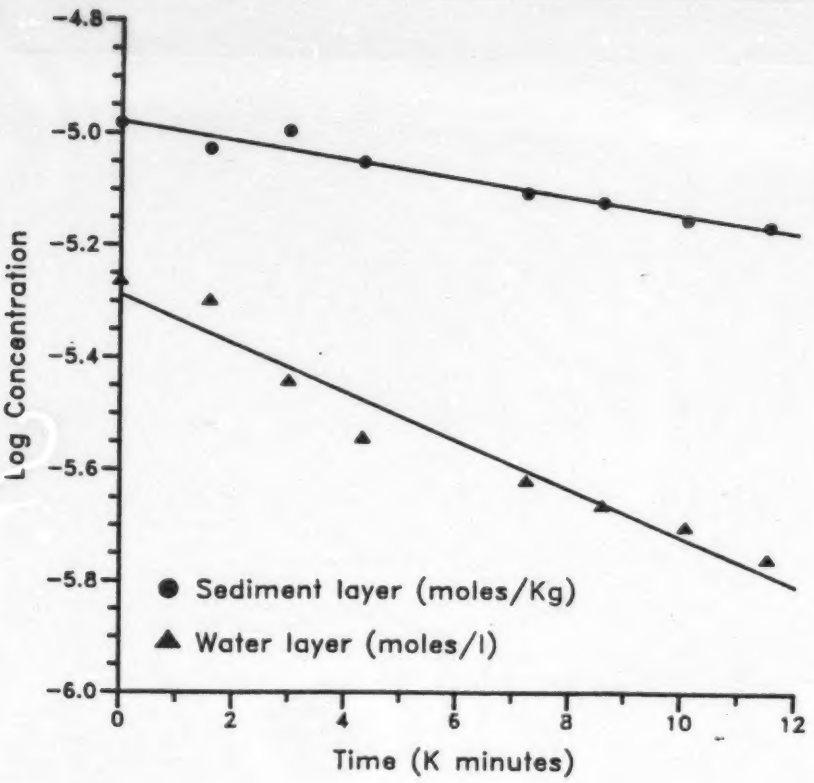

-4.8
-5.0
-5.2
-5.4
-5.6
-5.8
-6.0
Log Concentration
0
2
4
6
8
10
12
Time (K minutes)
Sediment layer (moles/Kg)
Water layer (moles/l)

Figure 5.

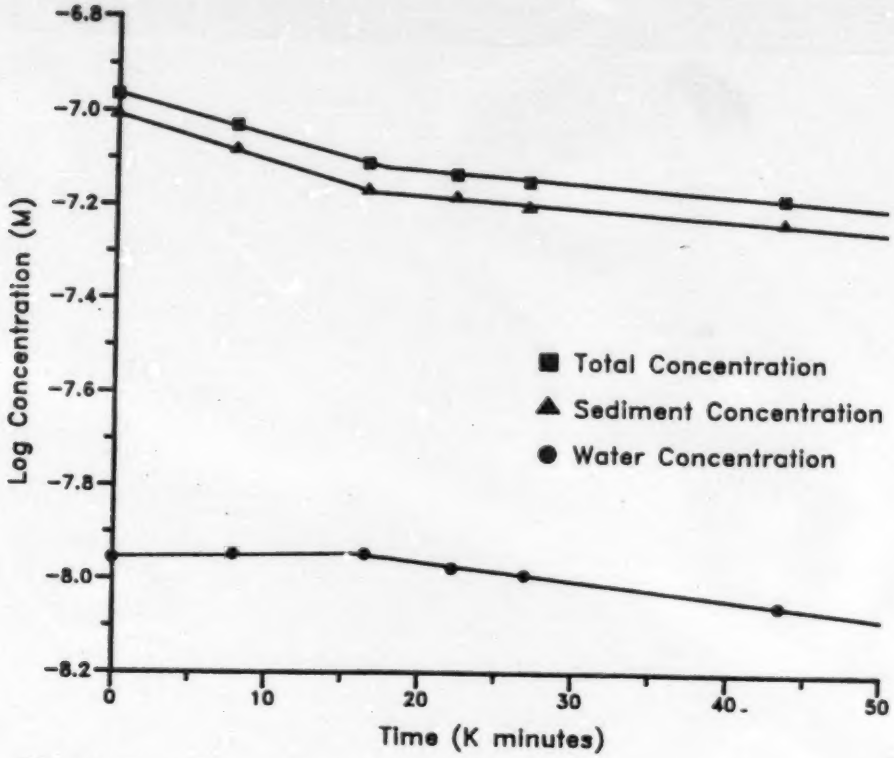

-6.8
-7.0
-7.2
-7.4
-7.6
-7.8
-8.0
-8.2
Log Concentration (M)
0
10
20
30
40
50
Time (K minutes)
Total Concentration
Sediment Concentration
Water Concentration

Figure 6.

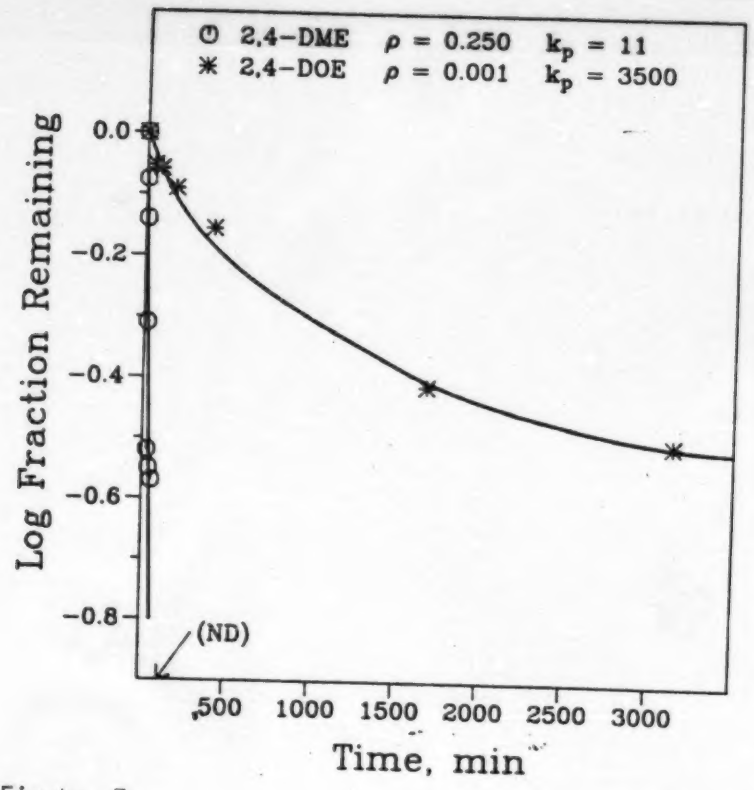

2,4-DME ρ = 0.250 k_p = 11
2,4-DOE ρ = 0.001 k_p = 3500
Log Fraction Remaining
0.0
-0.2
-0.4
-0.6
-0.8
(ND)
500
1000
1500
2000
2500
3000
Time, min

Figure 7.

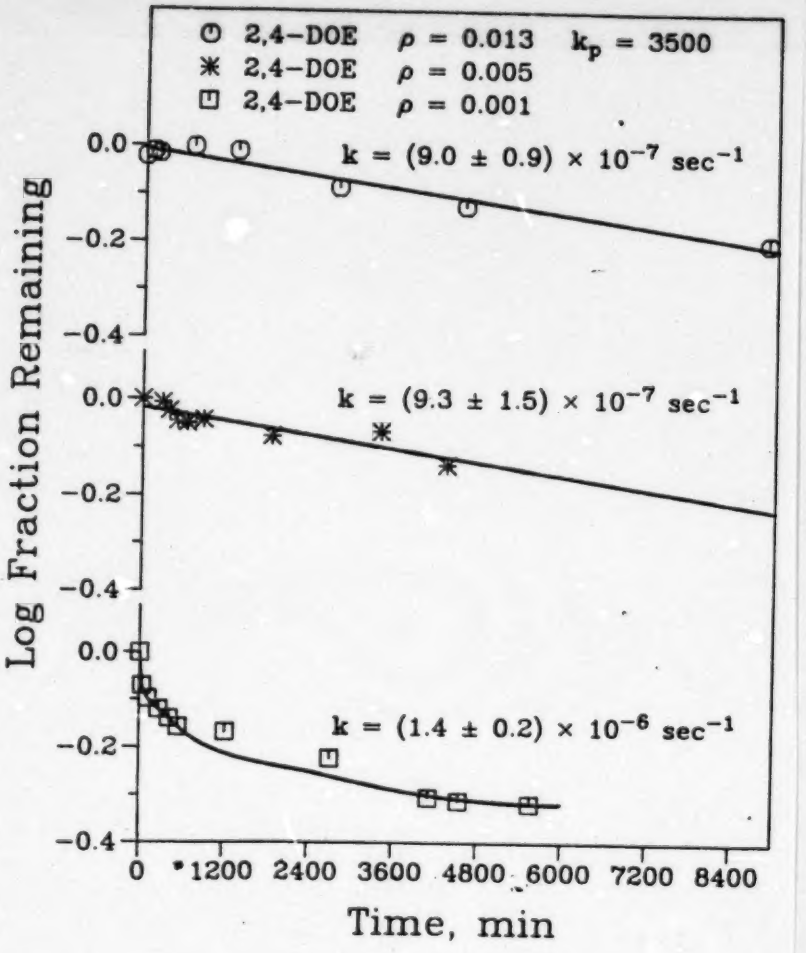

2,4-DOE ρ = 0.013 k_p = 3500
2,4-DOE ρ = 0.005
2,4-DOE ρ = 0.001
k = (9.0 ± 0.9) × 10^{-7} sec^{-1}
k = (9.3 ± 1.5) × 10^{-7} sec^{-1}
k = (1.4 ± 0.2) × 10^{-6} sec^{-1}
Log Fraction Remaining
0.0
−0.2
−0.4
0
1200
2400
3600
4800
6000
7200
8400
Time, min

Figure 8.